AN INVESTIGATION OF THE MECHANISM OF ELECTROLYTIC VALVE ACTION

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Shortly after the discovery of the irregular action of aluminum in an electrolytic cell by Wheatstone in 1855, Buff noted that when an alternating current is passed into an electrolytic cell, one electrode of which is aluminum, the current is rectified. This anomaly attracted a great deal of attention and has been investigated by many. The more extended investigations of recent times have been by Greene[1], Guthe[2], Fitch[3], Schulze[4], and Smits[5].

The ideas of these five men fall into two general classes; Fitch and Schulze contending that the action of the aluminum rectifier is largely, if not entirely, electronic in character. By electronic is meant that the anions never come in contact with the metal of the anode, but when they reach the oxide film upon the aluminum anode, due to the large fall of potential thru the film, the electron which constitutes the charge upon the anion breaks thru the film to the anode and the resultant atom is liberated out of contact with the anode. On the other hand, Greene, Guthe and Smits believe that the phenomenon is due to the selective penetration of the film by the ions. All of them recognize the fact that capacity effects play a considerable part in the action.

Greene points out that the rectifier does not act like an ordinary condenser. The results obtained by him lead him

to believe that the theory of ionic diffusion is correct.

Guthe notes that an increase in temperature increases the ammount of current which can pass under a given fall of potential. This he attributes to an increase in ionic velocities. He points out that certain anions, notably chlorine, pass the film without much resistance. Summing up he says, "We have a kind of semipermeable membrane which allows certain ions to pass and give off their electrical charges, while it prevents the passage of other kinds of ions."

Guthe studied the action of a membrane of copper ferrocyanide deposited in the walls of a porous cup. He passed direct current thru this in both directions and noted its anomalous behavior. He raised the question whether or not this action is analogous to that of the aluminum rectifier. He did not try alternating currents on this membrane, but states that his investigations indicate that further research would be of interest.

Fitch, while believing that the action of the aluminum rectifier is largely electronic in character, makes this significant statement," Any electrolyte which liberates oxygen on electrolysis can be used,---------it is only necessary that the metal form a compound with the liberated oxygen which has a rather high resistance."

Schulze states that if the only action present were ionic, that is to say, if the action were due only to the passage of the ions thru the film, no rectification could

be obtained, while if the action were electronic, alternating currents up to the highest frequencies could be rectified.

PRELIMINARY

The theory of Schulze has been largely accepted as the correct explanation. It seemed, however, that it should be possible to produce rectification by means of a cell which offered no opportunity for electronic conductance.

For this purpose a film of copper ferrocyanide was deposited in the walls of a porous cup. This film was prepared by the method of Morse and Horne as modified by Findlay[6]. After building the film at a potential difference of 12 volts for 120 minutes, the current had fallen to 0.008 amperes. When the potential is held constant the current seems to approach some extremely low limiting value. See Plate II. On reversing the current thru the cell, (See Plate I, Fig I.) thus making the copper sulfate solution the catholyte, the current started at a low value, but quickly rose to a fairly constant high value. See Plate III, Curve I. On again making the potassium ferrocyanide the catholyte, and using the same potential as before, the current started at a higher value than it had ever attained in the other direction but rapidly fell off. See Plate III, Curve II. The rate of fall was approximately 100 times as fast as while the current was being passed in the same direction to form the membrane. Now this is strictly analogous to Schulze's ionic valve action. It is without doubt due to the selective passage of the ions thru the film. The high initial value of the current when

Key to Plate I

Fig I

A--Ammeter

V--Voltmeter

R--Reversing Switch

E--Platinum Electrodes

S--Copper Sulfate Solution (5%)

K--Potassium Ferrocyanide Solution (5%)

P--Porous Cup Containing Film

Fig II

G--Galvanometer with hot wire juncture to measure current

R--Motor driven commutator for reversing current

C--Copper Coulomb Meter

E--Platinum Electrodes

S--Copper Sulfate Solution (5%)

K--Potassium Ferrocyanide Solution (5%)

P--Porous Cup Containing Film

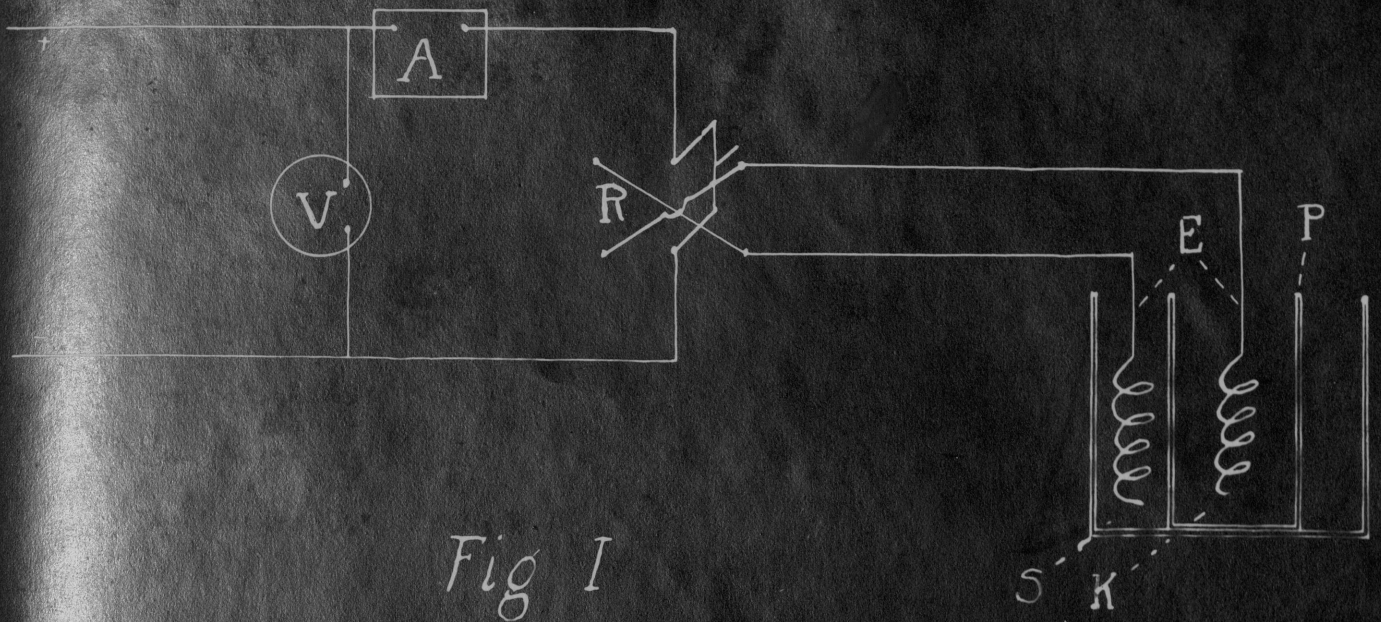


Fig I

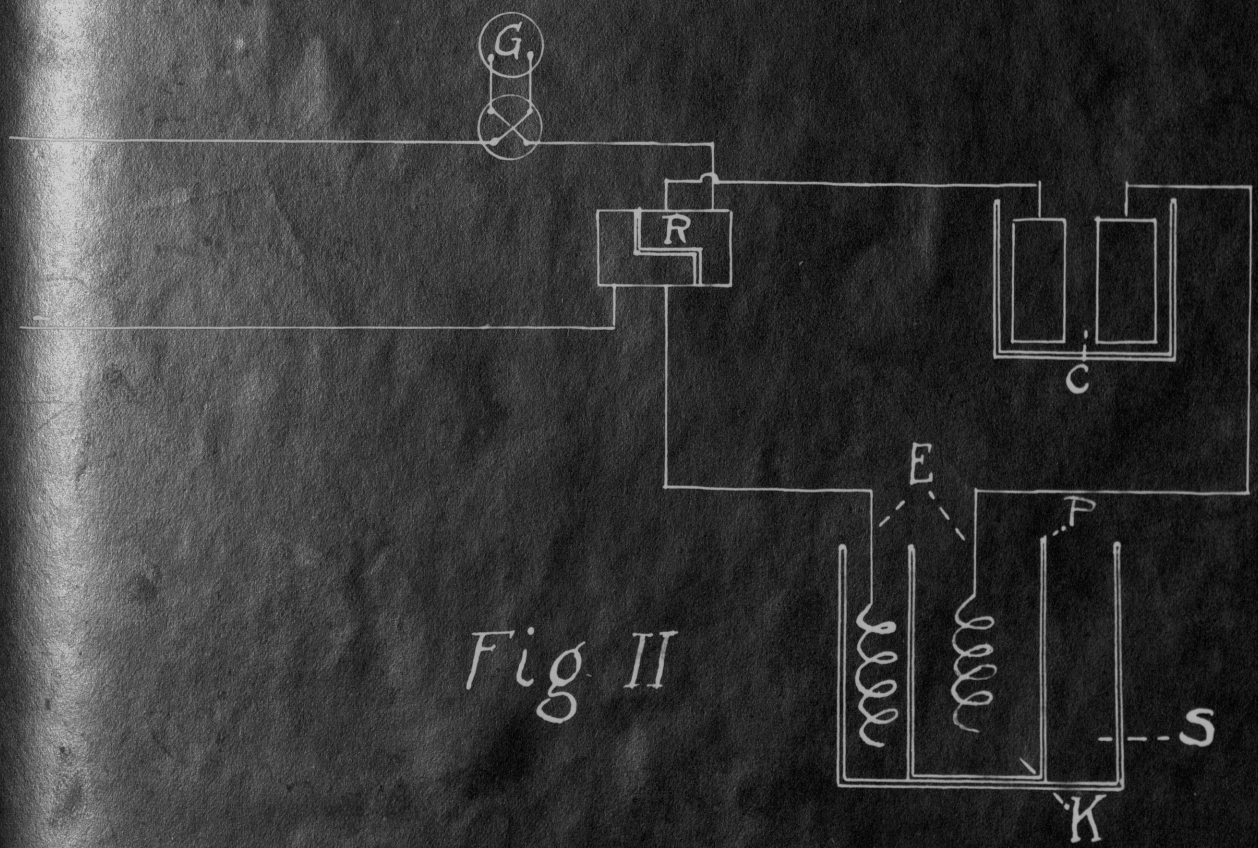
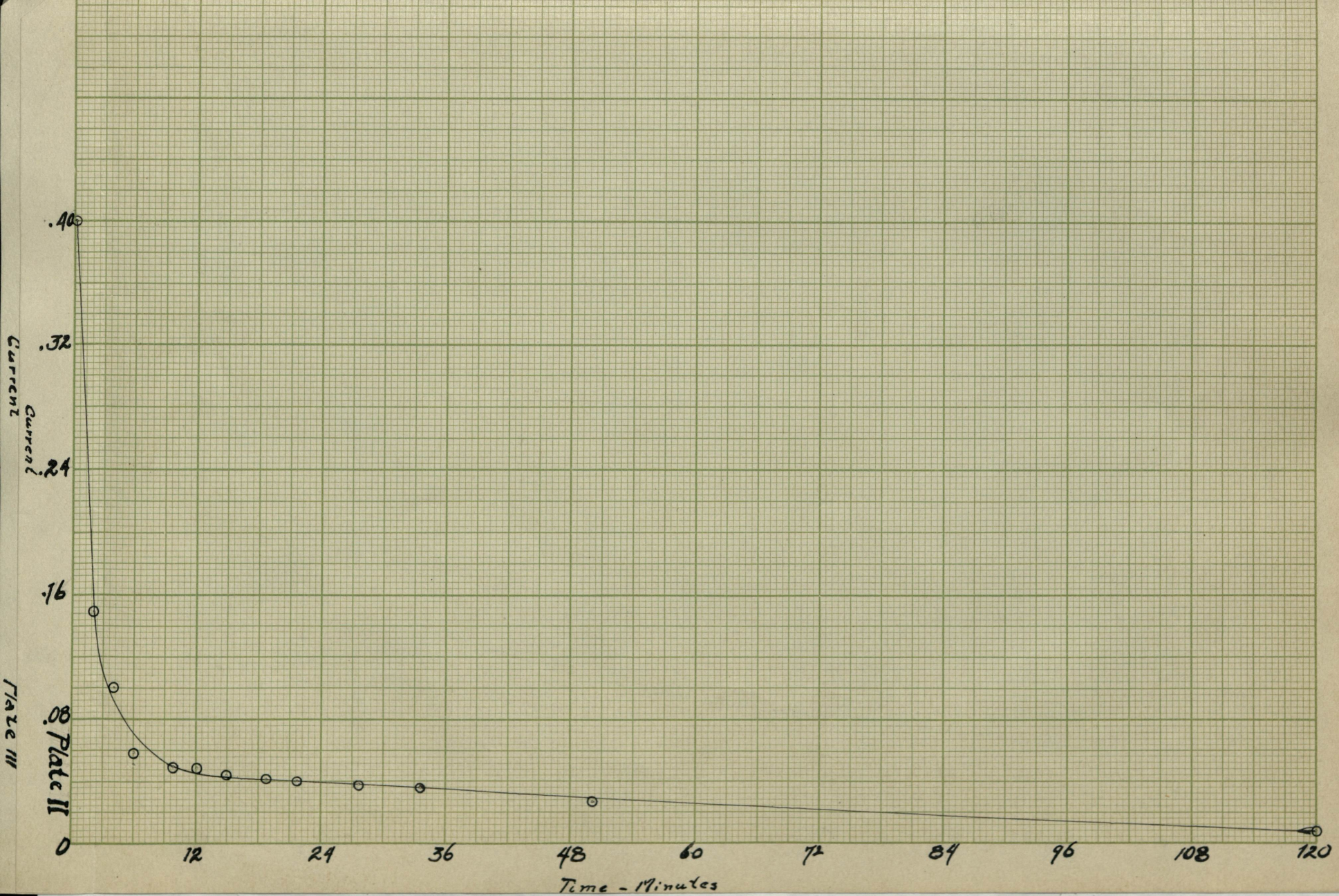


Fig II

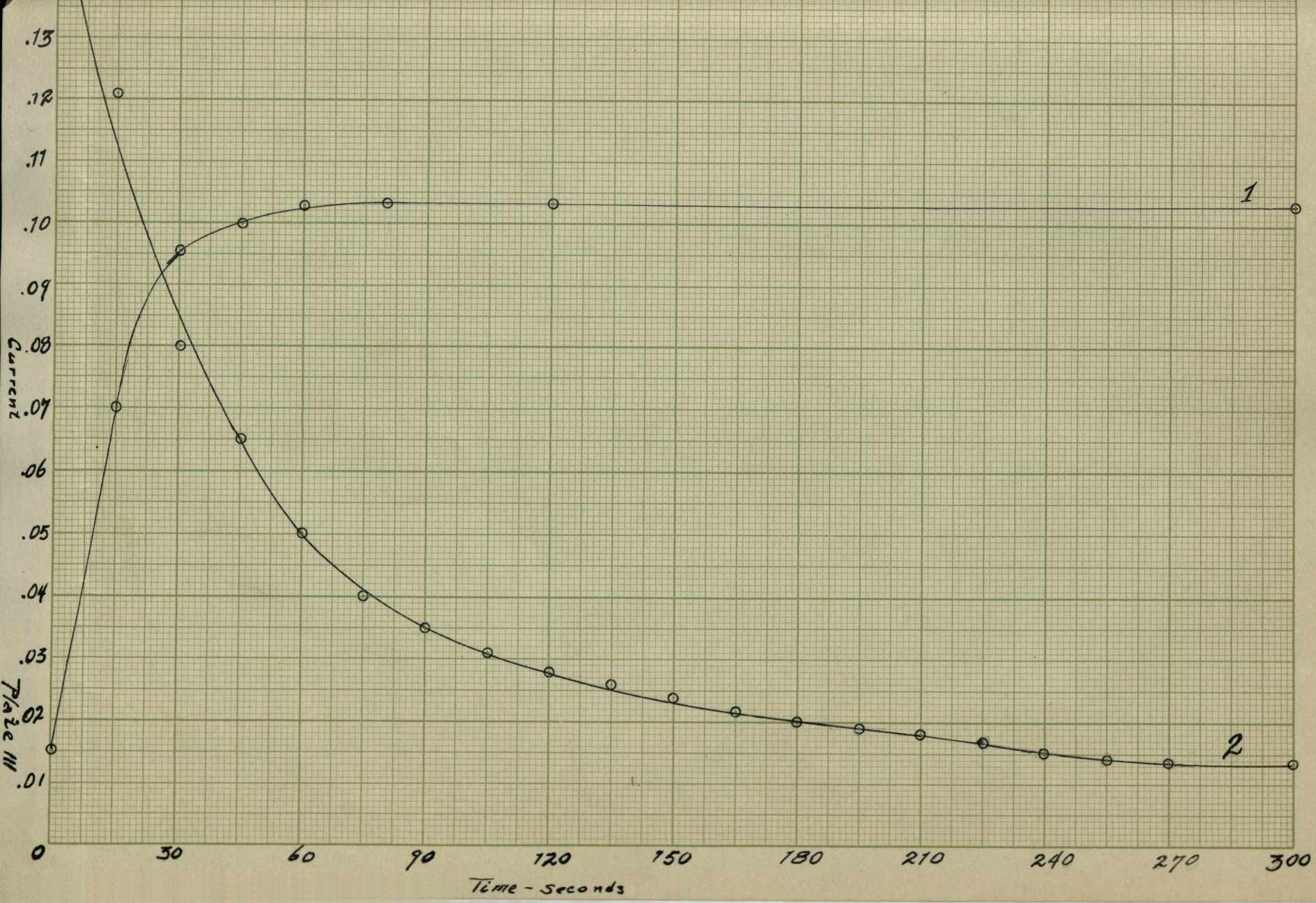
Plate I



Current

Plate III

Plate II


.13
.12
.11
.10
.09
.08
.07
.06
.05
.04
.03
.02
.01
0
Current
Plate III
30
60
90
120
150
180
210
240
270
300
Time - Seconds
1
2

the potassium ferrocyanide solution is the catholyte can only be explained by assuming the presence of all possible kinds of ions in the film at the start, for the initial value of the current in this direction is higher than the upper limit of the current in the opposite direction. Too, this high value persists too long to be due to a counter E.M.F. set up while the copper sulfate was the catholyte. This, and the following experiments were conducted using 5% solutions.

In order to determine whether or not this membrane would rectify an alternating current, a system was set up as shown in Fig II,Plate I,and a rectangular alternating current passed thru the cell and coulomb meter. The coulomb meter solution being acid,difficulty was experienced because of the dissolution of the copper electrodes of the coulomb meter while the system was on open circuit, that is,during the time elapsing while the commutator segment insulation was passing the brushes, but as the plates were of the same area and from the same piece of copper, it was assumed that they dissolved at the same rate.It was noted that there was more current passing in the direction in which the copper sulfate solution was the catholyte. The difference, which we may consider as the rectifying efficiency of the cell was about 6.5%. It appears to be independent of the number of cycles per second within the range used,(1.5 to 8 cycles per second) but increases with rise of temperature.This is due to the

increase of the ionic velocities with the increase of temperature.

The introduction of other electrolytes into either or both of the solutions,and the replacement of either or both gave quite uniformly lower efficiency or else entirely destroyed the action of the film. Among the substances used were ammonium hydroxide, di-ethyl ammonium hydroxide, cupric acetate,and acetic acid.

The work with this apparatus was so unsatisfactory and inaccurate that it was discarded and work undertaken using a General Electric Company oscillograph. It was found that the passage of time produced such changes in the film its self, that the period of observation must be extremely short to be of any value. No deductions will be drawn from the preliminary work as whatever might be said regarding it can be better shown from the oscillograms.

The Investigation Proper

When the cell Pt/Cu SO_4/$Cu_2Fe\ Cy_6$/$K_4Fe\ Cy_6$/Pt was used in the oscillograph circuit with an alternating current of 60 cycles per second, approximately the same rectification was obtained as at the lower frequencies of rectangular alternating currents. An examination of the oscillogram for this cell, the current and potential being upon separate axes, shows the sine form of the current being but little distorted. There is a lowering of the height of the waves, more in one direction than in the other, but only in a manner which would seem to be due to a purely ohmic phenomenon. See Plate IV, Fig I. The only explanation of this valve action is that it is due to selective penetration of the membrane by the ions. There can not be presumed to exist in the electrolyte any free electrons which might be responsible for the action. The algebraic sum of the velocities of the potassium and sulfate ions thru the film is greater by approximately 6.5% than is the algebraic sum of the velocities of the copper and ferro-cyanogen ions.

While the rectification of this cell is far from complete, here is a case where rectification is due to a film which has none of the requirements enunciated by Schulze as necessary for the rectification of alternating current. It is not an insulating skin upon the electrode, and it can not be supposed to be filled with a gas. It can be readily seen that this action is not due to a back E.M.F., by observing the amplitude of the two sides of the potential wave. The E.M.F. of such a cell as we have here is much too low to

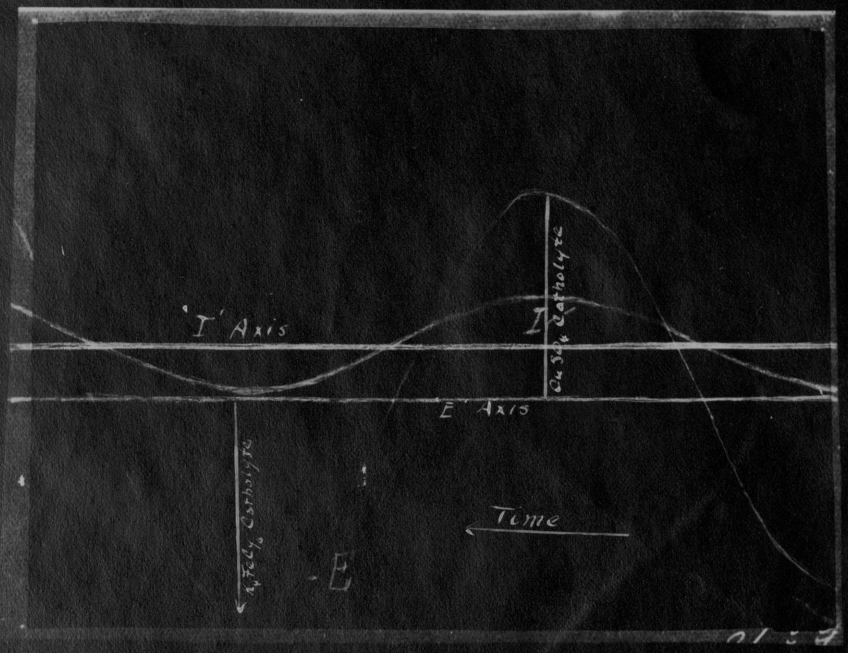


Fig I

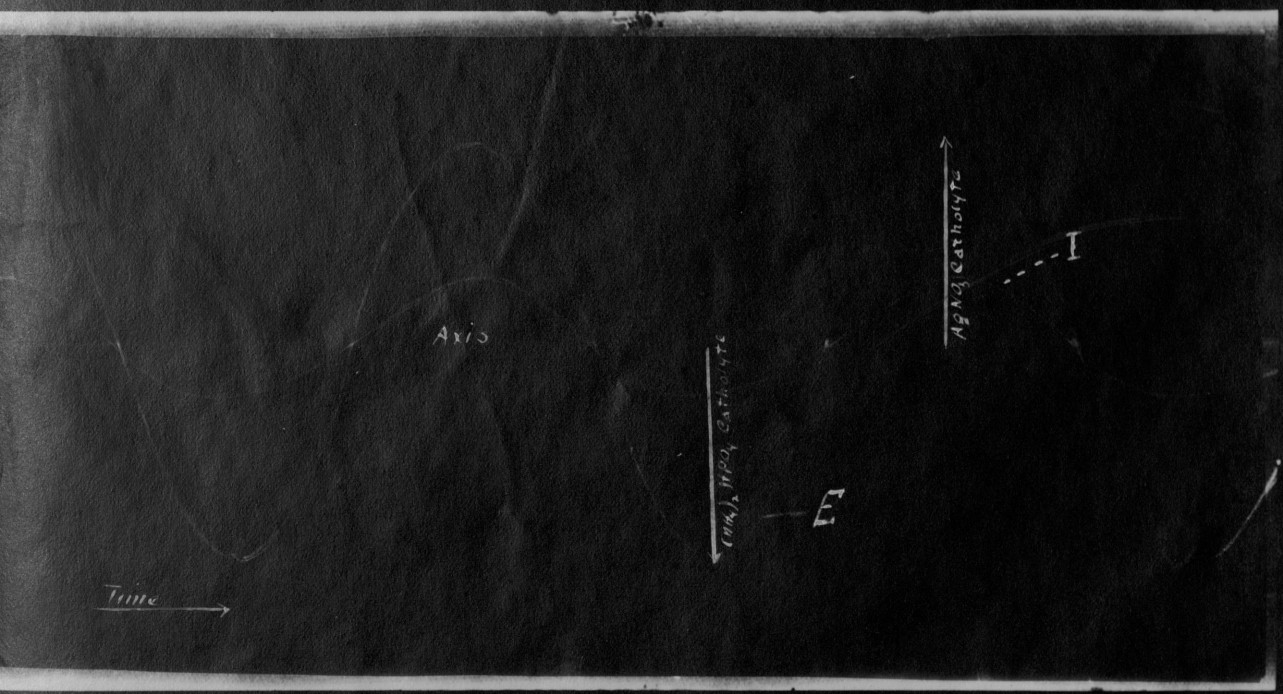


Fig II

to account for the action.[7]

Following out the line of reasoning involved here, that the action was due to selective ionic penetration, a film of silver phosphate was prepared in a manner analogous to the copper ferrocyanide film, using 5% solutions of silver nitrate and di-ammonium phosphate as the electrolytes and platinum electrodes as before. On imposing an alternating current of 15 volts potential, this film produced a much higher rectification than did the copper ferrocyanide film, approximately one third more current passing in the direction in which the silver nitrate solution was the catholyte than in the opposite direction. See Plate IV, Fig II.

It will be observed from the fact that the current leads the potential, that there is considerable capacity effect here. This is much more pronounced than in the copper ferrocyanide film, due to the greater dielectric character of the silver phosphate film and also to the presence of the hydrogen ion in the phosphate solution. The fact that the current reaches a maximum before the potential when the di-ammonium phosphate is the catholyte shows that the rectification is due to the selective penetration of the film by the ions. During the passage of the current in the direction in which the silver nitrate solution is the catholyte, the film is saturated with hydrogen, ammonium and nitrate ions; then when the current reverses, these ions are driven out and replaced by the silver and phosphate ions which pass thru the film with greater diff-

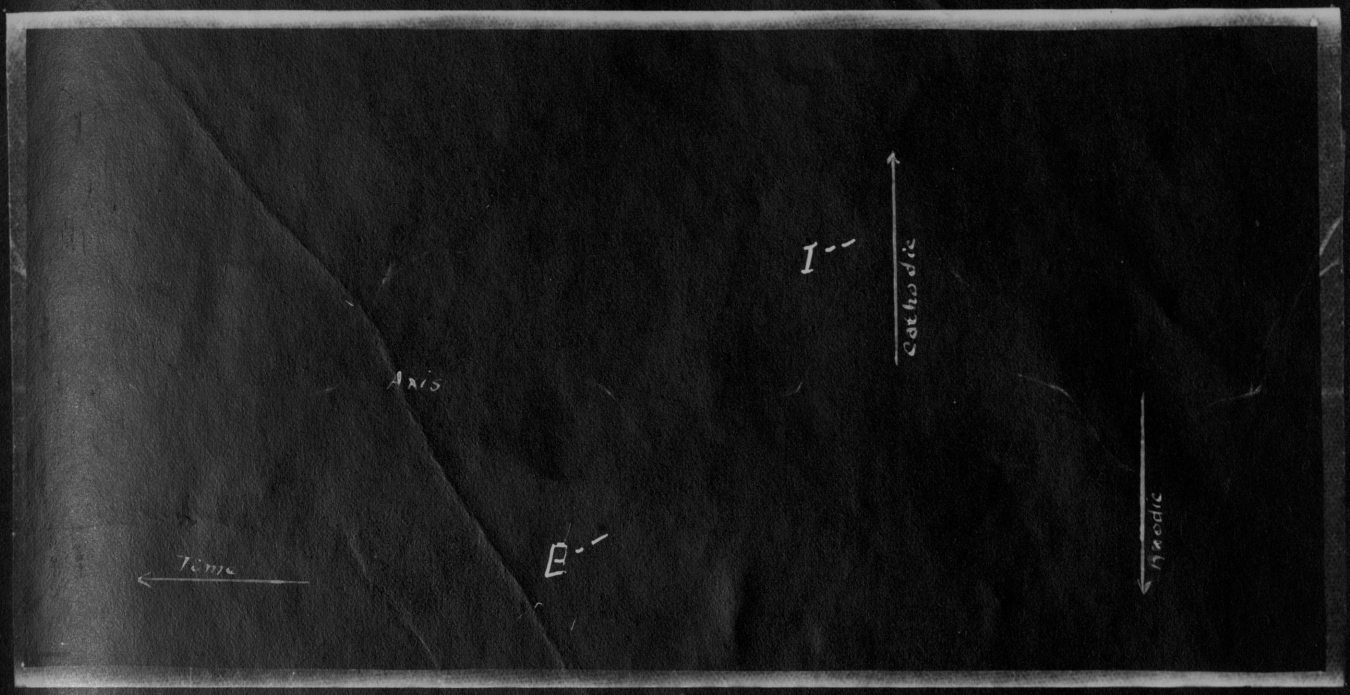


Fig I

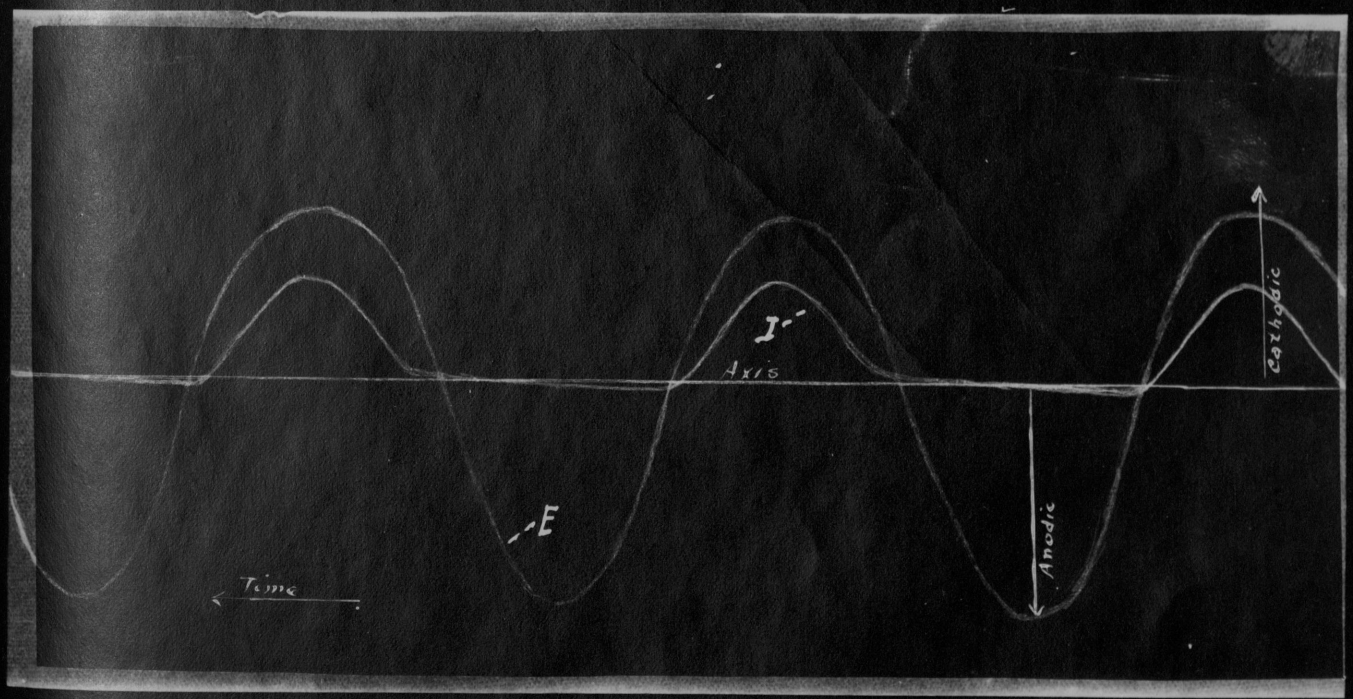


Fig II

iculty. Enough current has passed thru the cell to remove practically all of the hydrogen, ammonium and nitrate ions before the potential has reached a maximum. The falling off of the current while the current is still rising is the result. In other words, the algebraic sum of the velocities of the hydrogen, ammonium and nitrate ions thru the film is greater than is the algebraic sum of the velocities of the silver and phosphate ions. As a result, we have rectification. Due to the presence of the hydrogen, ammonium and nitrate ions in the film at the begining of the passage of the current in the direction in which the ammonium phosphate is the catholyte, we have a falling off of the current when these ions are depleted and replaced by the other pair of ions. The part which capacity effects play were without the scope of this investigation, but it appears that they are partially responsible, altho the major portion of the effect is due to the selective penetration of the film by the ions.

By analogy in appearance of the oscillogram of the silver phosphate film and the oscillogram of the film on an aluminum plate, it seems that there should exist an analogy between the mechanism of the action of the two electrolytic cells.

The oscillogram of a 60 cycle alternating current imposed upon an aluminum rectifier using di-ammonium phosphate as the electrolyte, is shown in Fig II, Plate V. Here again, and more noticeable than in the case of the silver

phosphate film,we have capacity effects manifested which cause the current to lead the potential.The current in the anodic direction with respect to the aluminum plate reaches a maximum almost immediately when the current starts.

Let us consider a complete cycle with this aluminum cell in the light of the analogy which seems to exist between the action of this cell and the cells in which the film is deposited in the walls of the porous cup. When the current starts in the direction making the aluminum the cathode, hydrogen and ammonium ions will tend to migrate thru the film and be discharged at the aluminum electrode. Due to the greater ease with which the hydrogen ion passes the film it will be discharged to a greater extent than will the ammonium ion.The presence of the small ammount of ammonium hydroxide formed at the electrode will have but little effect in dissolving the film of aluminum oxide. When the current reverses and the aluminum becomes the anode, there still remain in the film a large number of ions. The equilibriun $Al---Al^{+++}$ is rapidly set up and the cations migrate rapidly out of the film. The anions present in the film move toward the anode forming with the aluminum ion a difficultly soluble compound. When these ions in the film are depleted, nothing but the extremely small forming current can flow,due to the slow rate of passage of the anions into the film. This practically complete isolation of the anions from the electrode increases the capacity of the cell and as a result, we find that the

current leads the potential by about 1/750 of a second. On again reversing the current, thus making the aluminum the cathode, there are practically no ions in the film, so the current is initially low till the ions can migrate into the film under the potential drop across the cell. If the electronic theory is correct, why does not a definite difference of potential in the cathodic direction force as many electrons out of the metal at the begining of the half cycle as at the close?

In Fig I, Plate V is shown the oscillogram of an aluminum rectifier using di-sodium phosphate as the electrolyte. The reason for the large ammount of current carried in the anodic direction is probably because the sodium ions have penetrated the the film while the current was passing in the cathodic direction and have been discharged, the resulting sodium hydroxide dissolving the film on the aluminum. This is further evidence substantiating the theory that the action is ionic, for if the action were electronic, why should the effect be different simply because we change one ion in the electrolyte? Should not the aluminum give off its electrons at the same rate when the same potential difference is across the cell, irrespective of the change in the type of ions present? If the phemomenon is ionic, it is to be expected that two very mobile ions such as sodium and hydrogen should carry a

Fig I

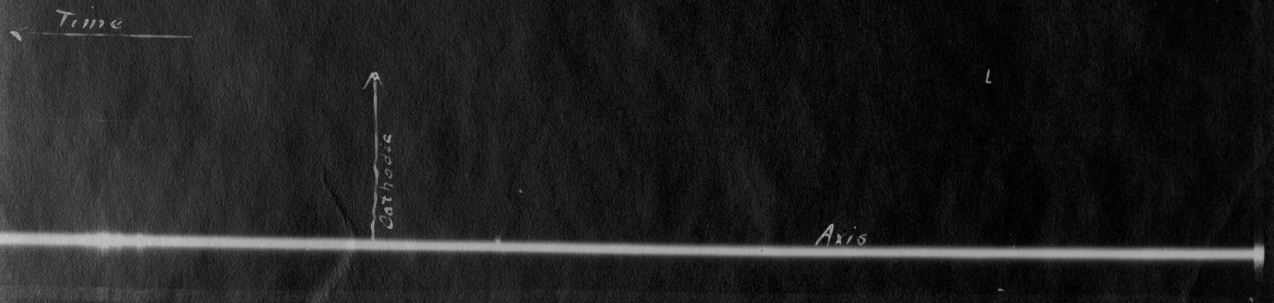


Fig II

Fig III

greater current thru the film than should hydrogen and the slower moving ammonium ion? If we trace a complete cycle thru this cell, we find that the ionic theory explains all observed phenomena while the electronic theory does not.

The validity of these deductions can be further seen by a study of the oscillograms on Plate VI, which were all produced using the same aluminum plate in a solution of di-ammonium phosphate and in each case under a difference of potential of 15 volts.

Fig I is the oscillogram of a rectangular potential of a frequency of 17.6 cycles per second. When the current starts in the cathodic direction there are present in the film but very few ions. Part of these are anions which migrated into the film while the current was passing in the anodic direction, and part are ions which diffused into the film during the period of open circuit, while the commutator segment insulation was passing the brushes. This period of open circuit was approximately 1/240 of a second. These ions migrate in their respective directions and the momentarily high current falls a little before they are replaced by the incoming cations. As the current continues, the number of ions which are driven thru the film increases till it reaches a definite limiting value at the potential used. This limiting value of the current is not realized at this frequency, but at a frequency of 4.7 cycles per second it is realized and the value of the current becomes constant.

Its value under a potential of 15 volts is 3.1 amperes. The film is impregnated with a large number of cations when the commutator again cuts off the current. During the period of open circuit a few more ions diffuse into the film and when the current starts in the anodic direction, it takes only about 1/700 of a second to completely wipe them out, and only a small forming current is then carried. This must be due to the anions which penetrate the film despite the resistance offered them. A study of this oscillogram aids in the understanding of why a greater current is carried in the cathodic direction on the falling side of the sine curve for an alternating current oscillogram than on the rising side. See Plate V, Fig II.

If the cell is allowed to stand for 20 minutes to permit as many as possible of the ions to diffuse into the film and the current then started in the cathodic direction, the oscillogram, Fig II, Plate VI, shows that the current rises a little, then falls to the limiting value of 3.1 amperes mentioned above. This shows than an important part is played by the ions, else why should the current behave in this manner. If the electron theory is correct, why does not a definite difference of potential force as many electrons out of the aluminum later that it does initially?

When a similar test is made, allowing 20 minutes for the film to become saturated with ions by diffusion and then the current started in the anodic direction, the current is initially high, but rapidly falls to an extreme-

ly low value, as shown in Fig III,Plate VI. This shows a marked similarity to curve 2 Plate III.

Summary

1. The preliminary work of this investigation shows the impracticability of any method of experimentation wherein appreciable time elapses during the taking of observations, due to the changes in the insulating film itself.

2. As it was without the scope of this investigation to determine the effect of capacity phenomena, no statement regarding this is offered than that capacity effects are present, and undoubtedly influence the ammount of rectification obtained.

3. The current carrying ability of the film increased during the period of open circuit in such a manner as to indicate that the conductance thru the film is largely ionic in character.

4. It appears that there is a strong analogy between the action of films which are interposed between the electrodes and those which are upon the electrodes, and in the former case, there is no reason for assuming that the conductance is electronic in character. Therefore the following theory is proposed.

Theory Proposed

The theory of ionic conductance explains more of the observed phenomena than does the theory of electronic conductance, so as Guthe has stated, it must be assumed that the rectification of the alternating current is due largely to the selective passage of ions thru the insulating membrane, which acts as a sort of a selective solvent permitting certain ions to pass freely while inhibiting the passage of others to a greater or lesser extent.

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